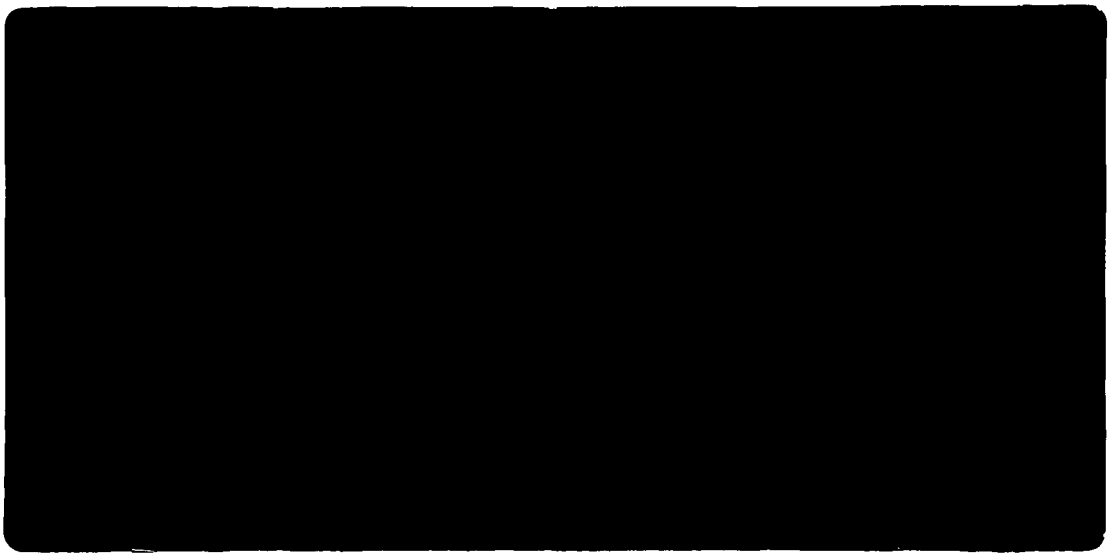
Institute of Paper Science and Technology
Atlanta, Georgia

IPST TECHNICAL PAPER SERIES



NUMBER 466

PHOTOYELLOWING OF MECHANICAL PULP PART 1: INHIBITION OF BRIGHTNESS REVERSION BY UNSATURATED COMPOUNDS

A.J. RAGAUSKAS

FEBRUARY 1993

Photoyellowing of Mechanical Pulp
Part 1: Inhibition of Brightness Reversion by Unsaturated Compounds

A.J. Ragauskas

To be published in
Tappi Journal

Copyright© 1993 by the Institute of Paper Science and Technology

For Members Only

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

Photoyellowing of Mechanical Pulp

Part 1: Inhibition of Brightness Reversion by Unsaturated Compounds

A.J. Ragauskas

Institute of Paper Science and Technology, Atlanta, GA, 30318.

ABSTRACT: The stabilization of bleached chemithermomechanical hardwood pulp against photoyellowing was studied. Impregnation of cyclic and acyclic diene compounds was shown to retard relative rates of brightness reversion. Experimental results demonstrated that the efficiency of stabilization is dependent upon the structure of the diene. Accelerated photo-aging studies suggest that trans,trans-2,4-hexadien-1-ol is as efficient as ascorbic acid at stabilizing mechanical pulp with respect to brightness reversion.

KEYWORDS: Brightness Reversion, Brightness Stabilization, Thermomechanical Pulp, Bleached Chemithermomechanical Pulp, Dienes

Introduction

Advances in mechanical pulping and bleaching have provided the means of manufacturing ultrahigh-yield pulps that have a Tappi brightness above 80%. At these levels of brightness, mechanical pulps could potentially be employed in high value paper products such as business forms, reprographic papers, and writing papers. However, the rapid light-induced yellowing of these brightened pulps restricts their use to short-life, low-

value paper products. It has been suggested by Cockram that, if the relative rate of light-induced yellowing could be reduced from three months, to 36 months the potential market for bleached CTMP would increase fourfold.[1]

The use of additives to retard brightness reversion of mechanical pulp has seen increasing attention. Early research efforts by Nolan and co-workers[2] demonstrated that the addition of near-UV absorbing compounds such as dihydroxy or tetrahydroxy-benzophenone could photo-stabilize mechanical pulp. Alternatively, the research efforts of Janson and Forsskahl[3] demonstrated the efficiency of several mercaptans to retard brightness reversion of high-yield pulps. These observations have been further pursued by Sarkanen[4] and Daneault et. al.[5] The use of ascorbic acid as an inhibitor of light reversion has also been explored. The effectiveness of this reagent and the proposed mechanism of photostabilization have been investigated by Heitner and others.[6] To-date, no one additive has met all of the market requirements needed to photostabilize mechanical pulp for commercial applications.

Based upon these photostabilization studies and others, we have initiated a survey study to identify novel methods of retarding brightness reversion. The principal focus of our studies has been the use of unsaturated cyclic and acyclic structures as antioxidants for high-yield mechanical pulps. The chemical literature suggests that unsaturated systems could stabilize mechanical pulp with respect to brightness reversion by several potential chemical mechanisms. In principle, olefinic additives could act as radical traps

for hydroxy and phenoxy radicals believed to be generated during photoyellowing of mechanical pulp.[7] Furthermore, photolysis studies by Schmidt et. al.[8] have demonstrated that conjugated dienes can act as triplet quenchers for the excited state of α-guaiacoxy-acetoveratrone and other lignin-like structures in protic solvents. These and other considerations suggest that the impregnation of mechanical pulp with olefinic additives could yield a novel method of photostabilizing mechanical pulp.

Results and Discussion

The effectiveness of the proposed stabilization reagents was evaluated by impregnating mechanical pulp handsheets with the additive and irradiating with a xenon-arc lamp. All irradiation experiments were carried out in triplicate, in the presence of three untreated handsheets. The brightness changes were monitored at specific intervals during irradiation. The stabilization effect of a given reagent on retarding brightness reversion of mechanical pulp was monitored by employing the % stabilization concept developed by Bailey and Lamont (Equation 1).[9]

% Stabilization = 100 x [(ΔBrightness of reference sample - ΔBrightness of treated sample)/Δ Brightness of reference sample]

Eq. 1

Our initial attempts at photostabilization of mechanical pulp employed 1-methoxy-1,3-cyclohexadiene (1,3-CHD), 1-methoxy-1,4-cyclohexadiene (1,4-CHD), and 1,2,4,5-tetramethyl-1,4-cyclohexadiene (TMCHD) impregnants for TMP handsheets. Preliminary studies with 1-methoxy-1,4-cyclohexadiene indicated that the % stabilization effect was

dependent upon the solvent the additive was dissolved in. A series of experiments established that methanol was the optimal solvent for impregnating handsheets with these dienes. The stabilization effect for 1-methoxy-1,4-cyclohexadiene was also shown to be dependent upon the application time and based strictly upon experimental convenience, all handsheets were treated with methanolic solutions for fifteen min.

Upon completing these preliminary experiments, research efforts were focused on determining the efficiency of photostabilizing TMP handsheets with the three cyclohexadienes. The results of these studies are summarized in Table I, and the data clearly indicate that 1-methoxy-1,3-cyclohexadiene and 1-methoxy-1,4-cyclohexadiene can reduce the rate of brightness reversion. These studies were then repeated employing bleached chemithermomechanical (BCTMP) hardwood pulp handsheets which had initial TAPPI brightness values above 80%. The results of the photostabilization studies, tabulated in Table I, and demonstrate that the use of the methoxycyclohexadienes can moderate the relative rate of brightness reversion for low- and high-brightness pulps.

Although these results were encouraging, the methoxycyclohexadienes were difficult to study due to the volatility of these structures. A carboxylic acid functional group should prevent volatilization of the inhibitor and enhance binding to the fibers; therefore handsheets of BCTMP were impregnated with 1,4-dihydro-2-methylbenzoic acid and photolysis studies were conducted (Table II). The data indicate that this diene is a moderately effective stabilizing reagent. As anticipated, the efficiency of photostabilization

was shown to be charge dependent. Furthermore, the % stabilization effect was found to be relatively stable over the four hours of photolysis, unlike the methoxycyclohexadienes. The differences in stabilization after four hours of irradiation were tentatively attributed to the differences in volatility of the compounds. Several other unsaturated cyclic system were examined, such as 1,3-cycloheptadiene, 1,3,5,7-cyclooctatetraene, 2-furoic acid, and furfuryl alcohol, but all of these compounds failed to retard relative rates of brightness reversion.

Research efforts were then focused on studying the photostabilization effects of acyclic unsaturated compounds. The initial additive examined was 2,4-hexadienoic acid. This compound was of interest since Robinson et. al.,[10] had reported it possessed mild antioxidant properties for mechanical pulp during bleaching and sheet drying. Accelerated photoaging studies suggested that the photostabilization effect for 2,4-hexadienoic acid was approximately 40% over a period of four hours, as summarized in Table II. A comparison of these results with those noted for 1,4-dihydro-2-methylbenzoic acid suggests that both additives provide comparable reductions in the relative rate of brightness reversion.

The photostabilization effect of 2,4-hexadienoic acid promoted our interest, and we initiated a study to determine if structural modification of this acid could enhance the observed effect. Preliminary studies indicated that the sodium salt of 2,4-hexadienoic acid actually accelerated brightness reversion. Furthermore, impregnation of 2,4-

hexadienedioic acid or 2,5-dimethyl-2,4-hexadienedioic acid onto BCTMP handsheets failed to significantly retard the relative rates of brightness reversion. Table II summarizes these results.

In contrast to these results, the application of trans,trans-2,4-hexadien-1-ol onto BCTMP handsheets was shown to be very effective at retarding brightness reversion, as reported in Table III. Accelerated photoaging studies demonstrated that a 5% application of the dienol on BCTMP handsheets afforded a % stabilization effect in excess of 80% after one hour of irradiation. Continued irradiation reduced the % stabilization effect to 75% after four hours, nonetheless this value was significantly larger than that noted for any other unsaturated systems studied. The photostabilization efficiency of trans,trans-2,4-hexadien-1-ol was evaluated by repeating the accelerated photoaging experiments in the presence ascorbic acid impregnated BCTMP brightness pads as reference handsheets. A comparison of the % stabilization effect for trans,trans-2,4-hexadien-1-ol and ascorbic acid indicated that both reagents were nearly equally effective in their ability to retard photoyellowing, as summarized in Figure 1. The application of both ascorbic acid and 2,4-hexadien-1-ol onto a BCTMP handsheet yielded handsheets which maintained a stabilization effect of approximately 73% throughout the four hours of irradiation in the solar simulator.

The successful commercial implementation of a photostabilization reagent for BCTMP and other ultra high-yield mechanical pulps is dependent upon several issues,

including thermal stability of the additive. The latter condition has imposed a serious challenge to the application of trans,trans-2,4-hexadien-1-ol for retardation of photo-yellowing. A series of long-term experiments indicated that the unsaturated alcohol impregnated onto BCTMP accelerates thermal reversion (see Table IV). The use of the mixture of ascorbic acid and trans,trans-2,4-hexadien-1-ol also exhibited accelerated long-term thermal reversion properties. Current research efforts are directed at understanding the important chemical mechanisms by which trans,trans-2,4-hexadien-1-ol contributes to accelerated thermal yellowing and photostabilization of mechanical pulp samples.

Conclusion

The results of these studies indicate that certain diene systems can retard the relative rates of brightness reversion for BCTMP hardwood pulps. The reduction in brightness reversion is dependent upon the chemical and physical properties of the additive. The most effective unsaturated system found to retard photoyellowing of BCTMP hardwood samples was trans,trans-2,4-hexadien-1-ol. Accelerated photoaging experiments suggest that this additive is as efficient as ascorbic acid in photostabilizing BCTMP handsheets. The value of the dienes as a commercial photostabilizer is questionable because the material appears to contribute to thermal reversion, nonetheless these results have suggested alternative methods of photostabilizing mechanical pulp and we are currently pursuing these avenues of research.

Experimental

Chemical

All solvents and reagents employed were commercial products and were used as received.

Pulp

Thermomechanical pulp was prepared by preheating juvenile southern pine chips for 10 min at 220 kpa saturated steam prior to refining in a two-stage Sunds Defibrator CD-300 pressurized first-stage refiner and a Defibrator ROP-20 atmospheric second-stage refiner.

BCTMP hardwood samples were obtained from a commercial source and used without further modification. Optical TMP and BCTMP handsheets were prepared according to TAPPI standards T-218 and T-205. After being air-dried in the dark at room temperature (22° F) and relative humidity (50%), the handsheets were washed in methanol to remove extractives. Removal of the extractives was required to allow for accurate determination of the amounts of additive applied onto the handsheets. Literature results[11] indicate that extractives do not contribute to photoyellowing of mechanical pulp, and their removal does not influence the overall rate of brightness reversion. After drying the handsheets under vacuum, brightness was measured according to Tappi standard T-452 and/or T-534. The handsheets were then soaked in a methanolic solution of the additive for 15 min and vacuum dried. After drying, the handsheets were re-equilibrated with room humidity and brightness values were measured. The amount of the additive

impregnated onto the handsheets was determined by weighing the handsheets before addition to the methanolic solution and after re-equilibrating the impregnated handsheets with room humidity. Reference handsheets were prepared in a similar manner except that they were not treated with the additive.

Accelerated Yellowing Studies

The accelerated photoaging studies were conducted with an Oriel 1000 Watt Solar Simulator. The Solar Simulator uses a xenon-arc lamp and was fitted with an air mass 1.5 global filter to model the average wavelength distribution of solar irradiation in the continental United States. An exhaust fan provided air circulation to minimize heating of the sample. Three impregnated handsheets and three reference brightness pads were placed 10.5" from the lens of the lamp and irradiated simultaneously. Immediately after photolysis the handsheets were stored in the dark until brightness values were recorded.

The long-term thermal reversion studies were accomplished at RT with the samples stored in a darkroom.

References

1. Cockram, R.A., CTMP in Fine Papers, Paper presented at the 1989 International Mechanical Pulping Conference, Helsinki, June, 1989.
2. a) Nolan, P.A., Paper Trade J. 121(23): 35(1945).

   b) Reineck, E.A.; Lewis, H.F., Paper Trade J., 121(20): 27(1945).
3. Janson, J., and Forsskahl, I., Nordic Pulp and Paper Res. J. 4: 197(1989).
4. Cole, B.J.W., and Sarkanen, K.V., Tappi J. 11(70): 117(1987).
5. Daneault, C., Robert, S., and Levesque, M., J. Pulp and Paper Science 17(6): J187(1991).
6. (a) Schmidt, J.A., and Heitner, C., J. Wood Chem. Technol. 11(4): 397(1991).

   (b) Fornier de Violet, P., Nourmamode, A., Colombo, N., Zhu, J., and Castellan, A., Cell. Chem. Technol. 24: 225(1990).
7. Agnemo, R., Francis, R.C., Alexander, T.C. and Dence, C.W., 1991 International Symposium of Wood and Pulping Chemistry Proceedings, TAPPI PRESS, Atlanta, p. 631.
8. Schmidt, J.A., Berinstain, A.B., Rege, D.E., Heitner, C., Johnston, L.J., and Scaiano, C., Can. J. Chem. 69: 104(1991).
9. Bailey, A.L., and Lamont, L.J., personal communication.
10. Robinson, J.C., Schroeder, M.A., Grimsley, S.A., and Jeffery, D.J., 1988 Pulping Conference, p 167.

11. Holmbom, B., Ekman, R., Eckerman, C., and Eckerman, C. 1989 International Symposium of Wood and Pulping Chemistry Proceedings, TAPPI PRESS, Atlanta, p. 445.

Table I. Photostabilization Effects for Mechanical Pulp Handsheets Treated with Methanolic Solutions of Cyclohexadienes.

	% Stabilization[a]					
Irradiation Time/h	1,3-CHD[b]		1,4-CHD[c]		TMCHD[d]	
	TMP	BCTMP	TMP	BCTMP	TMP	BCTMP
1	32	24	35	31	5	3
2	20	22	18	28	-5	2
4	3	7	-2	16	-3	2

[a]initial brightness values for TMP treated handsheets was 58.6 ± 1.8 (ISO) and for the BCTMP treated handsheets it was 86.0 ± 1.81 (Tappi);[b]1-methoxy-1,3-cyclohexadiene applied at 0.05 and 0.04 g/g of TMP and BCTMP handsheet, respectively;[c]1-methoxy-1,4-cyclohexadiene applied at 0.05 and 0.04 g/g of TMP and BCTMP handsheet, respectively;[d]1,2,4,5-tetra-methyl-1,4-cyclohexadiene applied at 0.06 and 0.02 g/g of TMP and BCTMP handsheet, respectively.

Table II. Photostabilization Effects for BCTMP Handsheets Treated with Methanolic Solutions of Unsaturated Acids.

Additive	Application Level (g/g handsheet)	Period of Irradiation (h)	% Stabilization[a]
1,4-Dihydro-2-methylbenzoic acid	0.02	1	27
		2	25
		4	23
1,4-Dihydro-2-methylbenzoic acid	0.17	1	57
		2	58
		4	58
2,4-Hexadienoic Acid	0.16	1	40
		2	42
		4	44
2,4-Hexadienoic Acid, Sodium Salt	0.04	1	0
		2	-1
		4	-9
2,4-Hexadienedioic Acid	0.03	1	20
		2	14
		4	11
2,5-dimethyl-2,4-Hexadiene-dioic Acid	0.06	1	8
		2	11
		4	14

[a]initial Tappi brightness for treated handsheets was 86.3 ±1.1.

Table III. Photostabilization Effects for BCTMP Handsheets Treated with Methanolic Solutions of trans,trans-2,4-Hexadien-1-ol and Ascorbic Acid.

Additive	Application Level (g/g handsheet)	Period of Irradiation (h)	% Stabilization[a]
2,4-Hexadien-1-ol	0.03	1	56
		2	51
		4	49
2,4-Hexadien-1-ol	0.05	1	88
		2	78
		4	75
Ascorbic acid	0.03	1	56
		2	52
		4	49
Ascorbic acid & 2,4-Hexadien-1-ol[b]	0.06	1	74
		2	74
		4	72

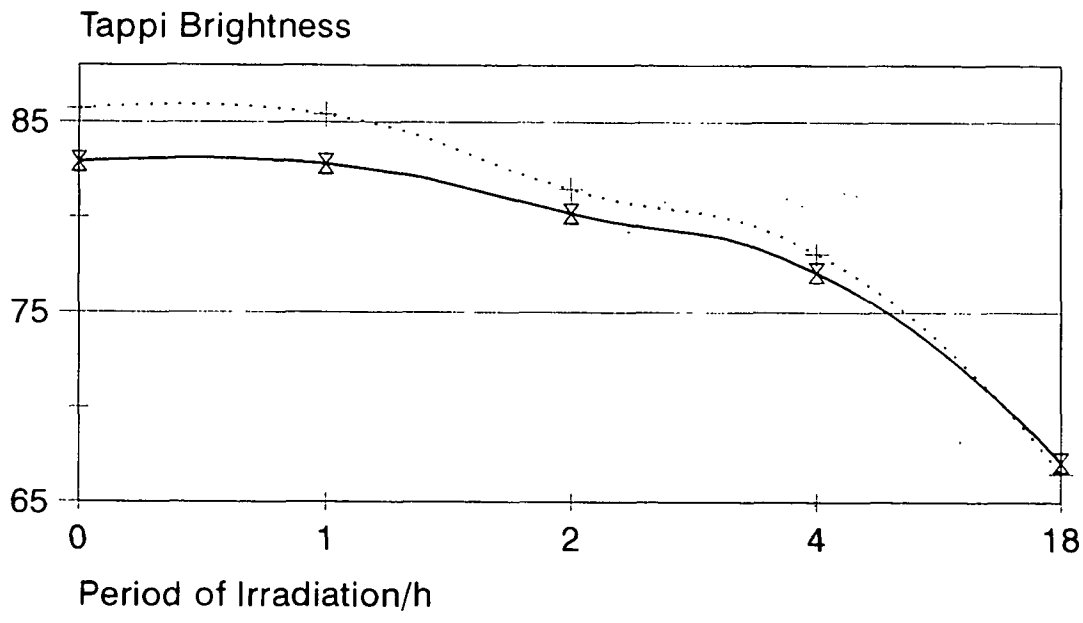
[a]initial Tappi brightness for treated handsheets was 87.0 ±0.7; [b]handsheets were soaked in a 0.01 M methanolic solution of trans,trans-2,4-hexadien-1-ol and ascorbic acid.

Table IV Thermal Reversion Effects for Treated and Untreated BCTMP Handsheets[a]

	Tappi Brightness For BCTMP Handsheets		
Days in Darkroom	Untreated	2,4-Hexadien-1-ol	2,4-Hexadien-1-ol & Ascorbic Acid
0	87	88	87
3	87	85	86
8	86	86	83
19	86	81	--
33	86	--	75
87	85	76	62

[a]handsheets were soaked in either a 0.09 M methanolic solution of trans,trans-2,4-hexadien-1-ol or a 0.09 M methanolic solution of trans,trans-2,4-hexadien-1-ol and ascorbic acid.

Figure 1: Comparison of the Photostabilization Effects for trans,trans-2,4-Hexadien-1-ol and Ascorbic Acid Impregnated BCTMP Handsheets[a]



[a]impregnated handsheets were photolyzed simultaneously; each handsheet had 0.03 g of additive/g of handsheet

Acknowledgements.

The author wishes to thank Ms. Tucker and Ms. Sacks for their technical assistance. This work was supported by the member companies of the Institute of Paper Science and Technology.